

## EVALUATION OF MORDENITE CATALYSTS FOR PHENANTHRENE HYDROCRACKING

S. A. Qader, D. B. McComber and W. H. Wiser

Department of Mining, Metallurgical &amp; Fuels Engineering

The University of Utah

Salt Lake City, Utah 84112

INTRODUCTION

H-mordenite, in combination with hydrogenation catalysts, has been used in hydrocracking of different types of hydrocarbons. Voorhies and Hatcher<sup>1</sup> and Beecher et al.<sup>2</sup> used pd-H-mordenite in the study of kinetics of hydrocracking of C<sub>6</sub>, C<sub>8</sub> and C<sub>10</sub> paraffinic and naphthenic hydrocarbons. The hydrogen mordenite used had a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> of about 10. The reactions were found to be of first order with respect to hydrocarbon concentration and the activation energies of hexane, cyclohexane, n-decane and Decalin were found to be 48, 31, 33 and 25 kcal./mole respectively. Beecher et al.<sup>2</sup> also used hydrogen mordenite having a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> of greater than 50 in combination with palladium in the hydrocracking of n-decane and Decalin. The aluminum deficient catalyst combination was found to be over 4 times as active as pd-H-mordenite combination. Aluminum deficient H-mordenite (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 64) was also found to be more active in cumene cracking by Eberly and Kimberlin<sup>3</sup>. Qader et al.<sup>4,5</sup> studied the hydrocracking of naphthalene and anthracene over catalysts containing H-mordenite (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>:10) and oxides and sulfides of Co, Mo, Ni and W. The reactions were found to be of first order with respect to hydrocarbon concentration and the activation energies of naphthalene and anthracene hydrocracking were found to be 30.5 and 28.6 kcal./mole respectively. The anthracene hydrocracking data was also found to be compatible with the dualsite mechanism according to the Langmuir-Hinshelwood model. The hydrocracking of phenanthrene over catalyst combinations containing H-mordenites of 10, 50 and 100 silica-alumina ratios is presented in this paper.

EXPERIMENTAL

Phenanthrene of over 99.8 percent purity was hydrocracked in a batch stirred tank reactor of 1-litre capacity, shown in Figure 1. Twenty grams of phenanthrene, 7.5 grams of H-mordenite or silica-(low) alumina and 2.5 grams of WS<sub>2</sub> were used in each experiment. Hydrocracking was carried out in the temperature range 400°-500°C at a constant initial (cold) pressure of 1800 psi. The final (hot) pressures varied between 3000 and 3500 psi. The reactants and catalysts were heated to the experimental temperature in 25-35 minutes and the time when the temperature reached the experimental temperature was taken as zero reaction time as shown in Figure 2. The conversions at zero reaction times were determined by cooling the products immediately after the temperature reached the experimental temperature. It took 1-2 minutes to cool the products to below 300°C in all experiments. It was assumed that no reaction took place during the cooling cycle. Zero reaction time hydrocracking conversions varied between 1 and 5 weight percent of phenanthrene under the experimental conditions employed. Experiments were conducted at reaction times of zero time (as defined above), zero time + 20, zero time + 30 and zero time + 60 minutes. The conversions obtained in between zero reaction time and zero time + 60 minutes were used for evaluation of mechanisms and kinetics. The volume of initial hydrogen used in the reaction and the product gases were measured by a wet gas meter. The liquid product and the spent catalyst were recovered by washing all the reactor parts with acetone.

In experiments designed for calculating weight balances, a weighed quantity of Tetralin was used for recovering the liquid product and catalyst. Catalyst was then separated from the liquid by filtration, washed with acetone and dried at 110°C. The weight of the liquid product was then obtained by difference.

Weight of liquid product = (weight of Tetralin + Liquid Product + Catalyst as recovered from the reactor) - (Weight of initial Tetralin used for washing + weight of dried spent catalyst).

The weight of C<sub>1</sub>-C<sub>4</sub> gases formed was obtained from total volume of gaseous product and gas composition. The difference between initial hydrogen used in the reaction and hydrogen present in product gas was taken as hydrogen consumed in the reaction. The analyses of liquid and gaseous products were done by gas chromatographic techniques. Since phenanthrene molecule contains 14 carbon atoms, all compounds in the product containing 13 carbon atoms or less were taken as cracked products for calculating hydrocracking conversions. The mole percent hydrocracking conversions were obtained from liquid product analyses.

Mole percent hydrocracking conversion = (Sum of mole percentages of all components of the liquid product which is equal to 100) - (Sum of mole percentages of all components of the liquid product containing 14 carbon atoms).

This was done on the assumption that there will be no change in the liquid moles during the reaction since each mole of phenanthrene can yield only one mole of each component of the liquid product. The higher compounds reported include liquid product components which come out in the chromatographic analysis after phenanthrene and coke.

#### COKE DETERMINATION

The fresh and spent catalysts were heated in a muffle furnace at 600°C for 3 hours and the weight losses were determined. The difference between the weight losses of each used catalyst and the fresh catalyst was taken as coke formed during the reaction.

#### RESULTS AND DISCUSSION

##### Reaction Mechanism:

Hydrocracking of phenanthrene involves three main reaction steps of hydrogenation, isomerization and cracking as indicated by the product distribution data given in Table I. Phenanthrene first gets hydrogenated to di-, tetra- and octa-hydrophenanthrenes. The hydrophenanthrenes, then get isomerized to C<sub>14</sub> isomers. C<sub>14</sub>-isomers contain the same number of carbon atoms (14) as hydrophenanthrenes and they are formed from tetra- and octahydrophenanthrenes by the skeletal rearrangement of saturated six member rings of the latter to saturated five member rings with methyl groups attached to them. The C<sub>14</sub>-isomers contain one or two saturated five member rings. This skeletal rearrangement is analogous to the isomerizat-

ion of hydroanthracenes to C<sub>14</sub>-isomers as reported by Qader et al.<sup>5</sup>. The third reaction step is the hydrocracking of hydrophenanthrenes and C<sub>14</sub>-isomers to lower molecular weight compounds. The product distribution data given in Table I indicates that the initial products of hydrocracking are C<sub>13</sub>-isomers and naphthalenes. C<sub>13</sub>-isomers contain 13 carbon atoms and one five member saturated ring in the molecule and they are formed from C<sub>14</sub>-isomers by demethylation of the latter. The alkyl naphthalenes and naphthalene are formed by the hydrocracking of hydrophenanthrenes, and C<sub>14</sub>- and C<sub>13</sub>-isomers. The formation of naphthalenes and tetralins as the initial products of hydrocracking suggests that cracking is taking place in one of the side benzene rings of the hydrophenanthrenes, and C<sub>14</sub>- and C<sub>13</sub>-isomers. As cracking proceeds further, indans and alkyl benzenes are formed in the product. This suggests that indans and alkyl benzenes are formed from naphthalenes and tetralins by the occurrence of hydrogenation, isomerization and cracking reactions as reported earlier by Qader et al.<sup>4</sup>. The product distribution data obtained in this work suggest that phenanthrene hydrocracking takes place through the occurrence of a multistep mechanism of hydrogenation, isomerization and cracking as shown in Figure 3. The reaction is a very complex one and the mechanism presented in Figure 2 represents only the gross hydrocracking pattern. Somewhat similar mechanisms were earlier reported by Sullivan et al.<sup>6</sup> and Rumohr and Kölling<sup>7</sup>. Sullivan et al.<sup>6</sup> hydrocracked phenanthrene over a nickel sulphide on silica-alumina catalyst and found that the reaction took place partly by a similar mechanism as shown in Figure 3 and partly by two other mechanisms. Rumohr and Kölling hydrocracked phenanthrene over a nickel on alumina catalyst and reported that the reaction took place by a mechanism somewhat similar to the one shown in Figure 3.

#### KINETICS OF HYDROCRACKING

During hydrocracking, phenanthrene gets hydrogenated to hydrophenanthrenes which subsequently get isomerized to C<sub>14</sub>-isomers. The hydrophenanthrenes and C<sub>14</sub>-isomers will then crack to lower molecular weight compounds. All compounds of the product containing less than 14 carbon atoms are taken as cracked products in the calculation of hydrocracking conversions. The conversion data were evaluated by a simple first order rate equation (1) where "x" is mole fraction conversion of phenanthrene

$$\ln (1-x) = -KT + Q \quad (1)$$

(mixture of phenanthrene, hydrophenanthrenes and C<sub>14</sub>-isomers) and Q is a constant. The plots of equation (1) shown in Figures 4 and 5 indicate that the order of hydrocracking reaction is one with respect to phenanthrene concentration at constant hydrogen pressure. The first order rate constants were used in calculating Arrhenius activation energies as shown in Figure 6. Activation energies of 20.8 and 35.3 kcal./mole were obtained in the hydrocracking of phenanthrene over H-mordenite (10) + WS<sub>2</sub> and Silica-(low) alumina + WS<sub>2</sub> catalysts respectively. The activation energies indicate that the hydrocracking reaction is predominantly controlled by chemical processes. The first order rate constants of phenanthrene obtained over Mordenite and Silica-alumina catalyst systems were found to be represented by equations (2) and (3) respectively.

$$K_m = 2.6 \times 10^2 e^{-20,800/RT} \text{ min.}^{-1} \quad (2)$$

$$K_{SA} = 7.3 \times 10^6 e^{-35,300/RT} \text{ min.}^{-1} \quad (3)$$

#### ACTIVITIES OF CATALYSTS

Activities of catalysts depend upon reaction conditions and nature of reactants. Activities of catalysts can be evaluated and compared by reaction rates calculated from conversion data. The rate of a chemical reaction is very much influenced by the catalyst activity and it is necessary to keep the catalyst activity same throughout the reaction. In hydrocracking coke deposition takes place on the catalyst and reduces the available active sites which in turn reduces the activity. A large excess of catalyst is used in this work to insure availability of sufficient number of active sites during the reaction. Conversion data obtained on four different catalysts are shown in Figure 7 and the first order rate constants are used to represent catalyst activities. The activities of the catalysts varied in the order  $\text{H-M-50} + \text{WS}_2 \approx \text{H-M-100} + \text{WS}_2 > \text{Silica-(low)} + \text{WS}_2 > \text{H-M-10} + \text{WS}_2$  as shown in Table II. The activity of mordenite +  $\text{WS}_2$  catalyst system almost doubled when the silica-alumina ratio of mordenite increased from 10 to 50. The activities of mordenites with silica-alumina ratios of 50 and 100 were found to be same. The aluminum deficient mordenites were earlier found to be more active in the hydrocracking of n-decane and Decalin<sup>2</sup>. Though activity increased with silica-alumina ratio, the phenanthrene hydrocracking mechanism remained same as indicated by the product distribution data given in Table III.

#### COKE FORMATION

Conversion data shown in Figure 2 indicate that most of the coke was formed during initial stages of the reaction. After the deposition of initial coke, the activity of the catalyst probably gets equilibrated. This appears to be happening at the zero reaction time and the increase in coke deposition after the zero time is not very high. The coke data shown in Figure 8 indicate that the mordenite based catalysts produce less coke when compared to silica-alumina based catalyst. The silica-alumina ratio of the mordenite appear to be having some influence on coke yield. Catalysts with silica-alumina ratios of 50 and 100 yielded more coke when compared to catalyst with silica-alumina ratio of 10.

#### REACTIVITIES OF HYDROCARBONS

The reactivities of different polynuclear aromatic hydrocarbons are compared by their first order rate constants as shown in Figure 9 and Table IV. The data show that phenanthrene is less reactive when compared to naphthalene and anthracene and more reactive than pyrene. The reactivities varied in the order anthracene > naphthalene > phenanthrene > pyrene.

#### ACKNOWLEDGMENT

This work is supported by the Office of Coal Research and the University of Utah.

## LITERATURE CITED

1. Voorhies, Jr., A., Hatcher, Jr., W. J., Ind. Eng. Chem. Prod. Res. Develop., 8, 361 (1969).
2. Beecher, R., Voorhies, Jr., A., Eberly, Jr., P., Ind. Eng. Chem. Prod. Res. Develop., 7, 203 (1969).
3. Eberly, P. E. and Kimberlin, Jr., C. N., Ind. Eng. Chem. Prod. Res. Develop., 9, 335 (1970).
4. Qader, S. A., Sridharan, R., Hill, G. R., Abstracts, The Second North American Meeting of Catalysis Society, Houston, Texas, p. 75 (1971).
5. Qader, S. A., Chun Chen, L. and Mcomber, D. B., 165th National Meeting, American Chemical Society, Division of Petroleum Chemistry, preprints, 18, No. 1, 60 (1973).
6. Sullivan, R. F., Egan, C. J., Langlois, G. E., J. Catalysis, 3, 183 (1964).
7. Rumohr, V. C. and Kölling, G., Erdöl und Kohle-Erdgas-Petrochemie Vereinigt mit Brennstoff-Chemie, 25, No. 6, 309 (1972).

TABLE I. HYDROCRACKING PRODUCT DISTRIBUTION OF PHENANTHRENE  
PRESSURE: 1800 PSI (COLD)

Catalyst	WS <sub>2</sub> (2.5 gram)	H-Mordenite (7.5 gram)	WS <sub>2</sub> (2.5 gm) +H-Mordenite (7.5 gram)	
Temperature, °C	400	500	400	450
Reaction Time, Mins.	0+5	0+30	0+5	0+10
LIQUID PRODUCT				
COMPOSITION, WT. %				
Phenanthrene	66.89	82.04	40.37	64.00
Hydrophenanthrenes (Di-, Tetra-, and Octa-)	29.17	10.54	51.70	25.64
Hydrophenanthrene isomers (C <sub>14</sub> )	2.68	3.01	4.21	5.22
Hydrophenanthrene isomers (C <sub>13</sub> )	0.70	0.50	0.41	0.76
Naphthalenes and Tetralins	0.56	3.13	2.99	3.00
Indans	nil	0.78	0.32	0.11
Alkylbenzenes and benzene	nil	nil	nil	1.27

TABLE II. ACTIVITIES OF CATALYSTS  
TEMPERATURE = 450°C  
PRESSURE = 1800 psi (cold)

Catalyst	First Order Rate Constant, Sec. <sup>-1</sup>
H-M-10+WS <sub>2</sub>	12.8 x 10 <sup>-5</sup>
H-M-50+WS <sub>2</sub>	21 x 10 <sup>-5</sup>
H-M-100+WS <sub>2</sub>	21 x 10 <sup>-5</sup>
Silica-(low) Alumina + WS <sub>2</sub>	17 x 10 <sup>-5</sup>

TABLE III. HYDROCRACKING PRODUCT DISTRIBUTION OF PHENANTHRENE  
PRESSURE = 1800 psi (cold)

Catalyst	H-M-10+WS <sub>2</sub>	H-M-50+WS <sub>2</sub>	H-M-100+WS <sub>2</sub>
Temperature, °C	400	425	400
Reaction Time, Mins.	0+5	0+5	0+5
<u>LIQUID PRODUCT COMPOSITION, WT. %</u>			
Phenanthrene	40.37	81.95	74.90
Hydrophenanthrenes (Di-, Tetra-, and Octa-)	51.70	15.36	20.19
Hydrophenanthrene isomers (C <sub>14</sub> )	4.21	1.31	0.97
Hydrophenanthrene isomers (C <sub>13</sub> )	0.41	0.11	0.48
Naphthalenes and Tetralins	2.99	1.27	2.74
Indans	0.32	nll	0.72
Alkylbenzenes and Benzene	nll	nll	nll

TABLE IV. REACTIVITIES OF HYDROCARBONS

	TEMPERATURE: 450°C
	PRESSURE: 1800 PSI (COLD)
	First Order Rate Constant, Sec. <sup>-1</sup>
Hydrocarbon	
Anthracene	16.5 x 10 <sup>-5</sup>
Naphthalene	14.3 x 10 <sup>-5</sup>
Phenanthrene	12.8 x 10 <sup>-5</sup>
Pyrene	5 x 10 <sup>-5</sup>

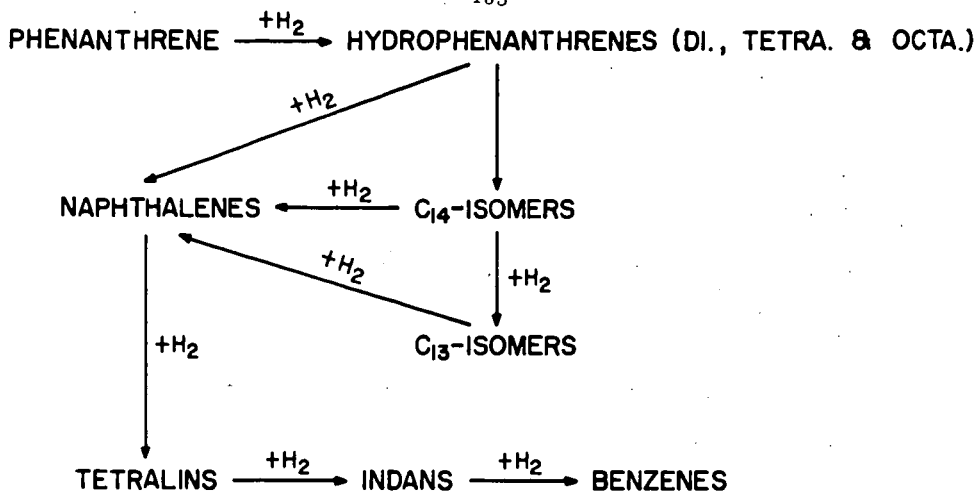
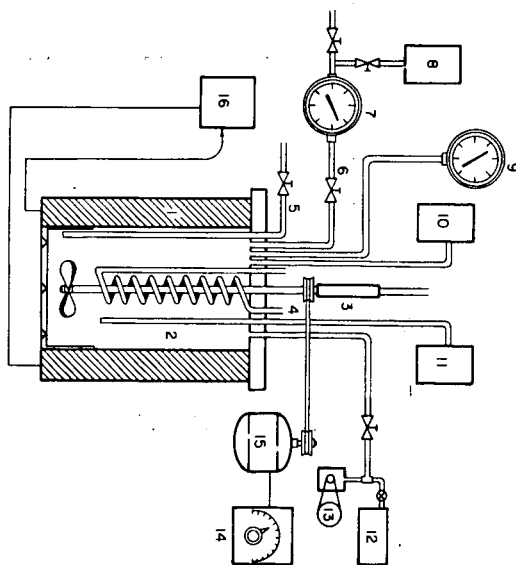


FIGURE 3. HYDROCRACKING MECHANISM OF PHENANTHRENE

FIGURE 1. BATCH STIRRED TANK REACTOR ASSEMBLY.



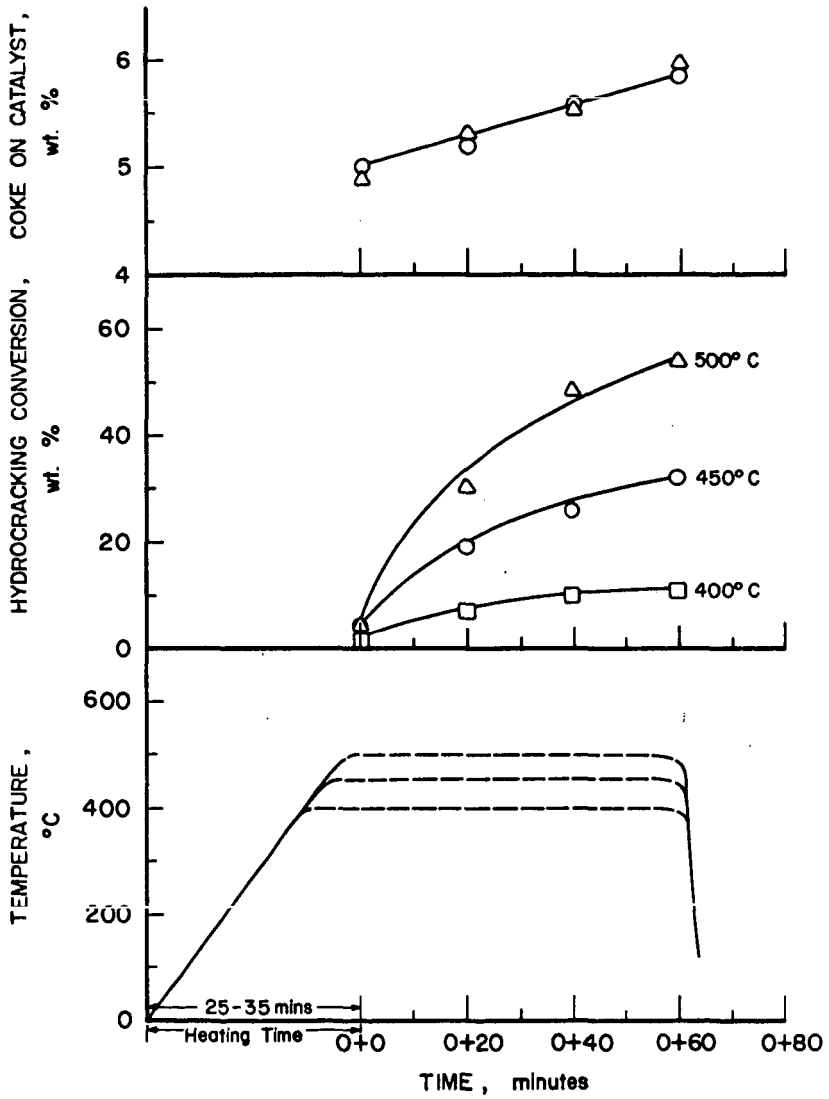


FIGURE 2. HEATING TIME - REACTION TIME - CONVERSION - COKE DEPOSITION



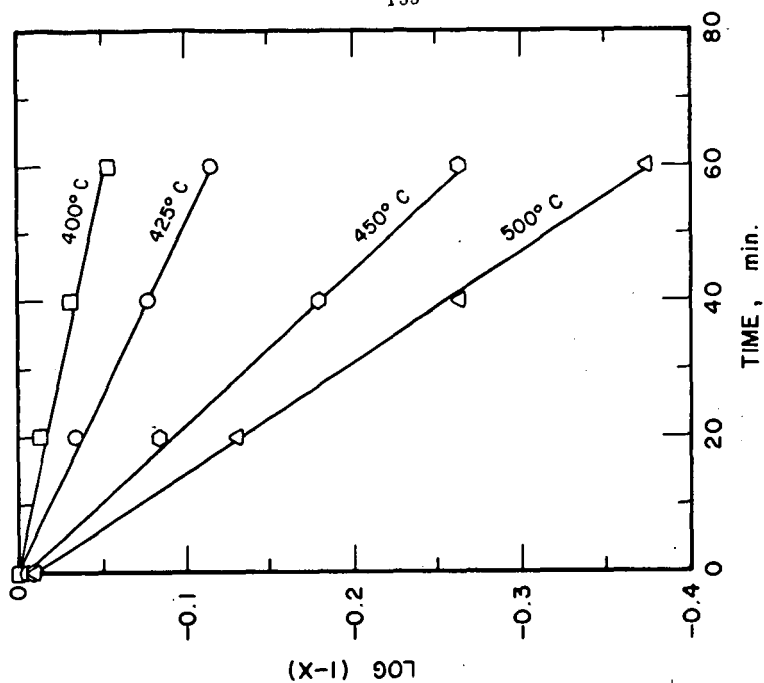


FIGURE 5. FIRST ORDER PLOTS-SILICA-(LOW) ALUMINA + WS<sub>2</sub>

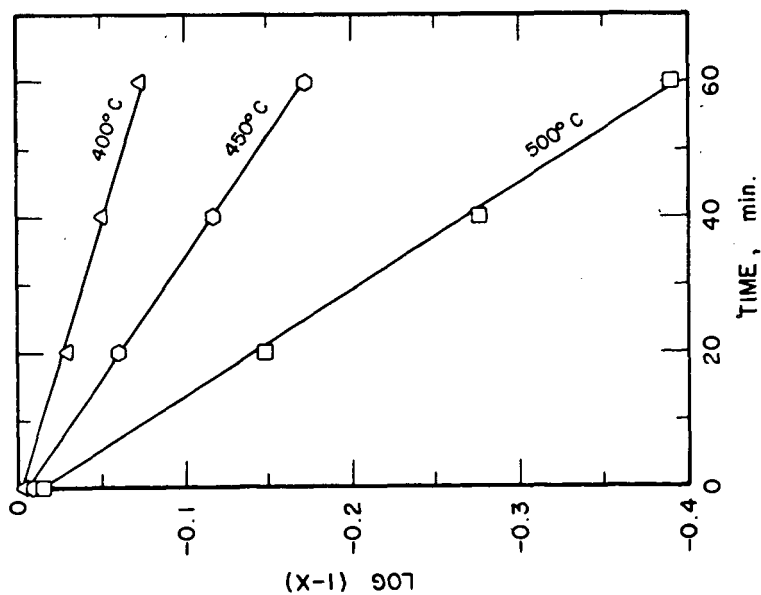


FIGURE 4. FIRST ORDER PLOTS-H-M-10+WS<sub>2</sub>

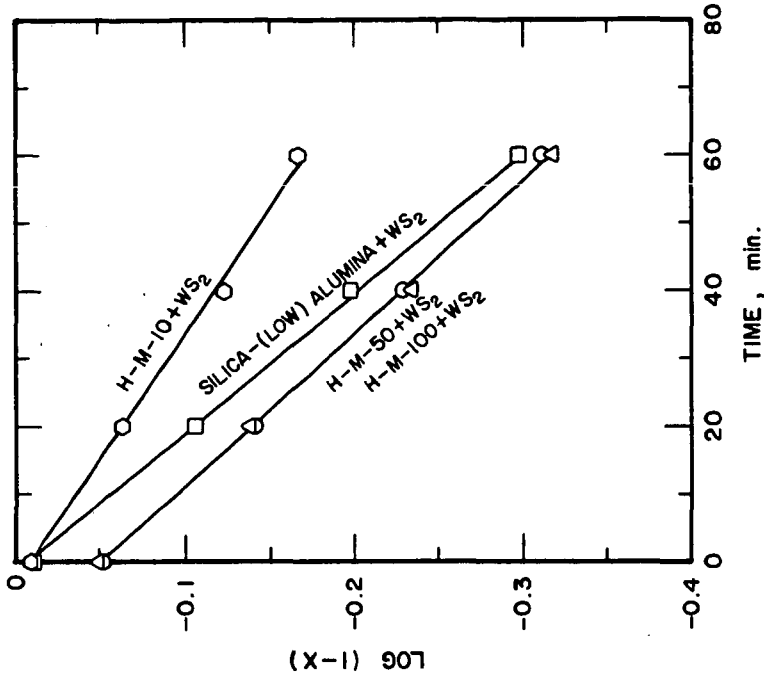


FIGURE 7. ACTIVITIES OF CATALYSTS  
TEMPERATURE: 450°C  
PRESSURE: 1800 PSI (COLD)

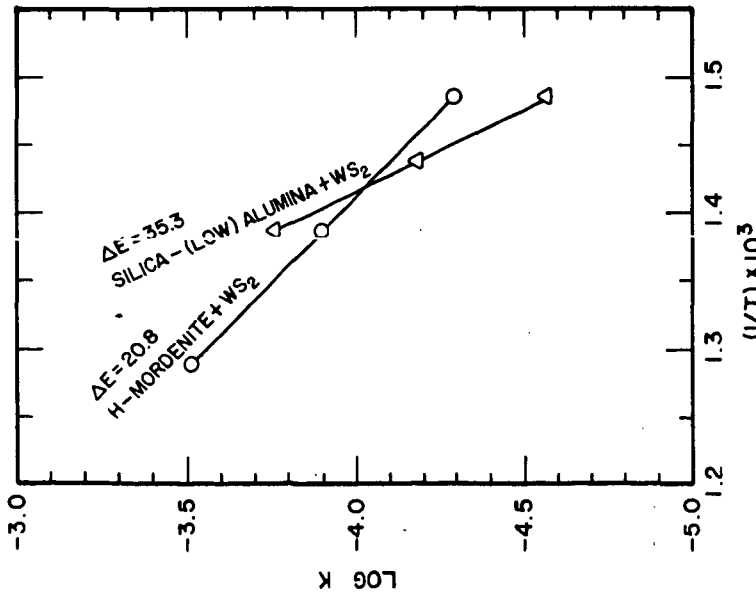


FIGURE 6. ARRHENIUS PLOT

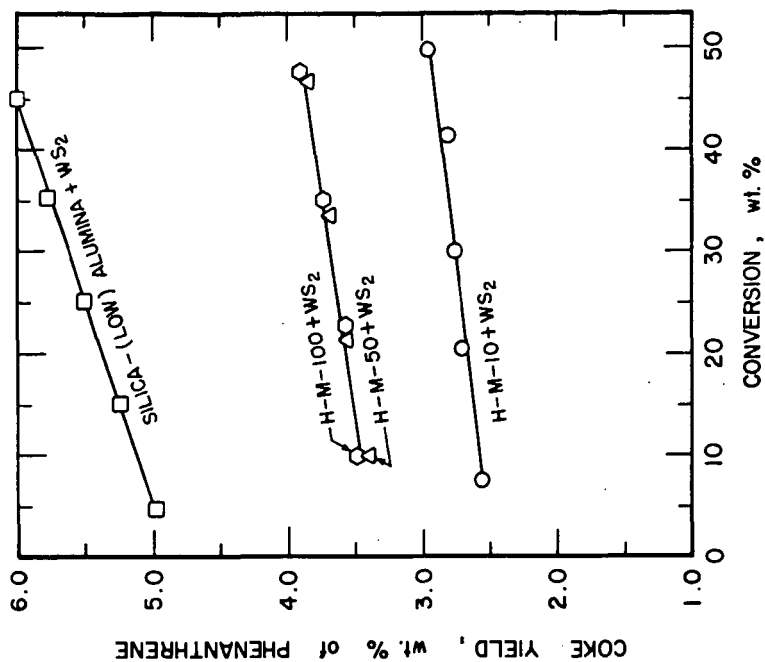


FIGURE 8. COKE YIELD DATA  
TEMPERATURE: 450°C  
PRESSURE: 1800 PSI (COLD)

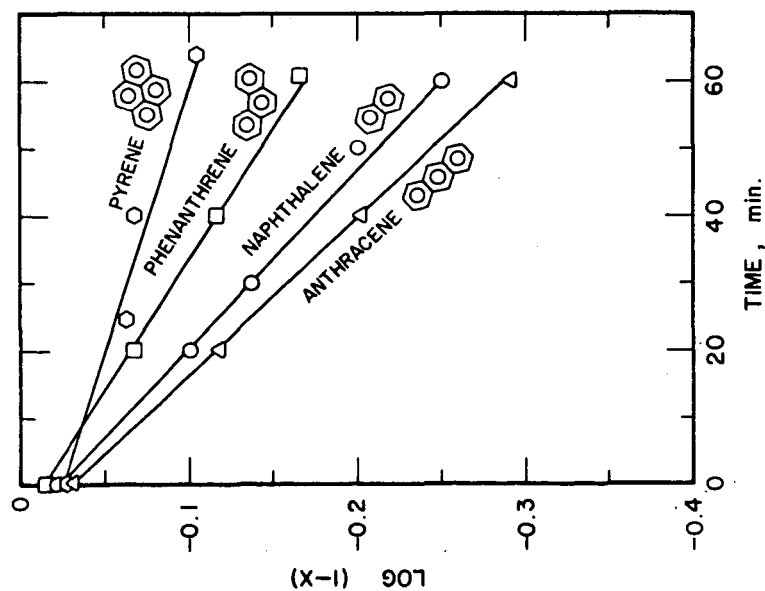


FIGURE 9. REACTIVITIES OF HYDROCARBONS  
TEMPERATURE: 450°C  
PRESSURE: 1800 PSI (COLD)